Influence of plasma pretreatment on shear bond strength of self-adhesive resin cements to polyetheretherketone

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Abstract: OBJECTIVES: The aim of this study is to evaluate the adhesion between PEEK and two self-adhesive resin cements after plasma treatment. METHODS: Eight hundred sixty-four polyetheretherketone (PEEK) disks were cut and polished to silicon carbide (SIC) P4000. One half of the specimens were randomly selected and pretreated with plasma, whereas the remaining 432 specimens remained untreated. Subsequently, specimens were randomly allocated to four groups ($n = 108$/group): Visio.link (Bredent), Signum PEEK Bond (Heraeus Kulzer), Ambarino P60 (Creamed), and a control group without additional treatment. Half of the specimens of each group ($n = 54$) were then cemented with either RelyX Unicem Automix 2 (3 M ESPE) or with Clearfil SA (Kuraray). All specimens were stored in water for 24 h (37 °C). Afterwards, specimens were divided into three groups ($n = 18$) for different aging levels: (1) no aging (baseline measurement), (2) thermal aging for 5,000 cycles (5/55 °C), and (3) thermal aging for 10,000 cycles (5/55 °C). Thereafter, shear bond strengths (SBS) were measured, and failure types (adhesive, mixed, and cohesive) were assessed. Data were analyzed using descriptive statistics, four- and one-way ANOVA followed by a post hoc Scheffé test ($p < 0.05$). RESULTS: No adhesion could be established without adhesive pretreatment, irrespectively, whether plasma was applied or not. Also, no bond strength was measured when Ambarino P60 was applied. In contrast, adhesive pretreatment resulted in SBS ranging between 8 and 15 MPa. No significant differences were found between the resin cements used. In general, no cohesive failures were observed. Groups without plasma treatment combined with Visio.link or Signum PEEK Bond showed predominantly mixed failure types. Control groups, plasma treated, or treated using Ambarino P60 groups fractured predominantly adhesively. CONCLUSION: The use of methyl methacrylate (MMA)-based adhesives allows bonding between PEEK and self-adhesive resin cements. Plasma treatment has no impact on bond to resin cements. CLINICAL SIGNIFICANCE: PEEK reconstructions can be cemented using self-adhesive resin cements combined with pretreatment with MMA-based adhesives.

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Clin Oral Investig

Influence of plasma pretreatment on shear bond strength of self-adhesive resin cements to polyetheretherketone

Short title: Bonding properties to PEEK and resin cements

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Keywords: PEEK, Plasma, adhesive, bond strength

Abstract

Objectives: To evaluate the adhesion between PEEK and two self-adhesive resin cements after plasma treatment.

Methods: Eight-hundred-and-sixty-four PEEK disks were cut and polished to silicon carbide (SIC) P4000. One half of the specimens was randomly selected and pre-treated with plasma, whereas the remaining 432 specimens remained untreated. Subsequently, specimens were randomly allocated to four groups (n=108/group): Visio.link (Bredent), Signum PEEK Bond (Heraeus Kulzer), Ambarino P60 (Creamed) and a control group without additional treatment. Half of the specimens of each group (n=54) were then cemented with either RelyX Unicem Automix 2 (3M ESPE) or with Clearfil SA (Kuraray). All specimens were storage in water for 24 h (37°C). Afterwards, specimens were divided into three groups (n=18) for different aging levels: i. no aging (baseline measurement), ii. thermal aging for 5000 cycles (5/55°C) and iii. thermal aging for 10000 cycles (5/55°C). Thereafter, shear bond strengths (SBS) were measured and failure types (adhesive, mixed and cohesive) were assessed. Data were analyzed using descriptive statistics, four- and one-way ANOVA followed by a post-hoc Scheffé test ($p<0.05$).

Results: No adhesion could be established without adhesive pretreatment, irrespectively whether plasma was applied or not. Also, no bond strength was measured when Ambarino P60 was applied. In contrast, adhesive pretreatment resulted in SBS ranging between 8 and 15 MPa. No significant differences were found between the resin cements used. In general, no cohesive failures were observed. Groups without plasma treatment combined with Visio.link or Signum PEEK Bond showed predominantly mixed failure types. Control groups, plasma treated or treated using Ambarino P60 groups fractured predominantly adhesively.

Conclusion: The use of MMA-based adhesives allows bonding between PEEK and self-adhesive resin cements. Plasma treatment has no impact on bond to resin cements.

Clinical Significance: PEEK reconstructions can be cemented using self-adhesive resin cements combined with pretreatment with MMA-based adhesives.

1. Introduction

Polyetheretherketone (PEEK) has been used in prosthetic dentistry as provisional abutment, implant, implant supported bar or clamp material in the field of removable dental prostheses (RDPs) [1-4]. It is a high-temperature semi crystalline thermoplastic polymer from the group of polyaryletherketone (PAEK) consisting of an aromatic backbone molecular chain, interconnected by ketone and ether functional groups [5] with the density of 1.3 – 1.5 g/cm^3. Its favorable biocompatible and mechanical properties [5-6], as well as a high melting point (about 343°C), good dimensional stability at high temperatures and chemical stability to nearly all-organic and inorganic chemicals makes it an interesting material for metal-free prosthodontics. One major drawback of PEEK is the greyish and opaque color and the requirement of veneering composites to achieve acceptable esthetics.

However, to achieve adequate bond strength between PEEK and resin composite materials are difficult due to its low surface energy and resistance to surface modification by different chemical treatments [7,8]. Currently, industry bonds elastomers to PEEK classically by conventional abrasive treatment, acid etching, plasma or laser techniques to prepare the engineering plastics surface followed by the application of epoxy adhesives. Knowledge concerning the potential and limitations of this material in adhesion to resin composites in the field of dentistry is still scarce. A first study on this topic assessed the bonding potential of a self-adhesive resin cement (RelyX Unicem) and an adhesive/composite system (Heliobond/Tetric) to differently pre-treated PEEK surfaces. It was show that bonding to PEEK was possible when using a bonding system on an etched surface using sulfuric acid [9]. Another study also indicated that bonding to PEEK can be achieved with composite resin in combination with an adhesive (Heliobond or Clearfil Ceramic Primer) when a self-adhesive resin cement was used [10]. However, etched PEEK surfaces using sulfuric acid resulted in increased initial bond strengths up to 21.4

MPa [10]. Both available studies used no artificial aging like thermo-cycling to challenge the bonding performance of dental resins to PEEK [9, 10]. In addition – from a clinical perspective – the use of sulfuric acid etching for chair-side PEEK abutment modification seems hazardous and should rather be avoided. Therefore, it remains unknown whether bonding to PEEK withstands the hydrolytic effects due to water absorption, which is known to dramatically reduce resin-bonding capacity to oxide ceramics [11-14]. An adequate long-term bonding durability would be a prerequisite for intraoral usage of bonded PEEK restorations. Therefore, further studies are still required and other means of simple and safe surface (pre-)treatment modalities are still desirable. Among the latter, plasma surface treatment might be a promising approach. It represents a process that raises the surface energy of different materials, which can lead to improved bonding characteristics. The physical definition of "plasma" is an ionized gas with an essentially equal density of positive and negative charges. An alternating electrical field at radio or microwave frequencies to electrodes can apply these changes. These excited molecules will decay and excite other species, which leads to an interaction with the surface in a dry chemical way, thereby forming a new surface layer. Typical gases used for treatment of polymers are air, oxygen, nitrogen, helium, argon and ammonia. The plasma can exist over an extremely wide range of temperature and pressure [15].

This in vitro study investigated the bond strength after plasma treatment and different adhesive material applications to two resin cements after different aging levels. The null-hypothesis was that plasma application would not improve the bond strength to resin cements.

2. Materials and methods

2.1 Specimens preparation

In this study, a material was used (Dentokeep PEEK Disc, nt-trading, Karlsruhe, Germany, Lot.No: 11DK18001), which represented a ceramic filled (20%) polyether ether ketone (Figure 1). Blanks were sectioned to the geometry of 5x5 mm and a thickness of 2 mm with a low-speed diamond saw (Well 3032-4, Well Diamantdrahtsägen, Mannheim, Germany). The resulting 864 specimens were embedded in an acrylic resin (ScandiQuick, ScanDia, Hagen, Germany) and then polished first to SIC P400 and then to P4000 with an automatic polishing device (Tegramin-20, Struers, Ballerup, Denmark) for 60 s under water-cooling. Subsequently, all specimens were ultrasonically cleaned (Sonorex RK102H, Bandelin electronic Berlin, Germany) in distilled water for 5 min and then air-dried. Four-hundred-and-thirty-two specimens were left untreated whereas the remaining 432 specimens were pretreated with cold active inert gas plasma for 20 s at a pressure of 200 kPa from a distance of 10 mm (Piezzobrush, Reinhausen Plasma, Regensburg, Germany). All plasma treatments were performed directly before the luting of specimens.

The specimens were then randomly divided into the following groups (n=108/group; Table 1):

(A) Visio.link

(B) Signum PEEK Bond I + II

(C) Ambarino P60

(D) No adhesive material (control)

One half of each group (n=54) was luted with the self-adhesive resin cement RelyX Unicem Automix 2 (3M ESPE, Seefeld, Germany, Lot.No: 475760) and the other half (n=54) with Clearfil SA (Kuraray Medical Inc, Sakazu, Kurashiki, Okayama, Japan, Lot.No: 033BBA). Specimens were secured in a special holding device as described in detail in a previous study [9]: In short, the resin cements were placed in an acrylic mold (inner diameter: 2.9 mm; D+R Tec, Birmensdorf, Switzerland) with a resin thickness of 1.5 mm and polymerized according to the manufacturer`s instruction. Subsequently, all luted specimens were stored in water for 24 h at 37°C and then randomly allocated to 3 subgroups with respect to different aging levels (n=18): One group was tested immediately after the 24 h of water storage, both other groups were thermally cycled for 5,000 cycles or 10,000 cycles, respectively. Thermocycling was performed between 5°C and 55°C (dwell time: 20 s) in an automated thermocycling machine (SD Mechatronik, Feldkirchen-Westerham, Germany).

2.2 Shear Bond Strength (SBS)

After thermocycling, SBS was tested in a Universal Testing Machine (Zwick 1445, Zwick, Ulm, Germany) at a crosshead speed of 1 mm/min. Specimens were positioned in the jig of the testing machine with the PEEK surface parallel to the loading direction. The bond strength was calculated with the following formula: Force to failure / Bonding area (MPa=N/mm^2).

2.3 Failure types analyses

Three failure types were defined and determined as follows: a) adhesive (no resin cement remnants left on the PEEK surface), b) mixed (resin cements remnants partially left on PEEK with PEEK surface exposed), and c) cohesive failure in PEEK. All failure types were evaluated by one calibrated examiner, who was unaware of the group allocation and treatment, under an optical microscope (Axioskop 2 MAT, Karl Zeiss Mikroskopie, Göttingen, Germany).

2.4 SEM analyses

Two additional PEEK specimens were polished up to 1 µm with a diamond suspension (Struers, Ballerup, Denmark) and then ultrasonically cleaned in isopropanol. One of the specimens was plasma treated as described above. The untreated surface was protected from the plasma effect with an adhesive foil, which was later removed for SEM analysis. The specimens were then gold sputtered and surface topography was evaluated under a scanning electron microscope (SEM, Carl Zeiss Supra 55 VP Gemini, Carl Zeiss, Oberkochen, Germany) operating at 10 kV with a working distance of 5.0-6.0 mm.

2.5 Statistical analyses

Power analysis was calculated using nQuery Advisior (Version 6.0, Statistical Solutions, Saugaus Mass) prior to performing this study. A Pilot study for resin cement RelyX Unicem to PEEK was used [9]. A sample size of 18 in each group will behave 95% power to detect the decrease by 25% of the mean (4.75 MPa) caused by aging, assuming that the common standard deviation is 3.8 MPa using two group t-test with 0.05 two-sided significance level.

For statistical data analysis of results obtained in this study, descriptive statistics such as mean, standard deviation (SD) and 95% confidence intervals (95%CI) were calculated. Normality of data distribution was tested using Kolmogorov-Smirnov and Shapiro-Wilk tests. Four-way ANOVA with respect to plasma treatment, adhesives, resin cements and aging level and one-way ANOVA regarding the adhesives followed by the Scheffé post-hoc test was used to determine significant differences between groups for each aging level separately. Relative frequencies of failure types together with the corresponding 95%CI estimated according to the Ciba Geigy tables were provided. P values smaller than 5% were considered to be statistically significant in all tests. These data were analyzed using SPSS Version 20 (SPSS INC, Chicago, IL, USA).

3. Results

Table 2 presents the descriptive statistics for shear bond strength values and the results of one-way ANOVA with Scheffé post-hoc test for each aging level separately.

The four-way ANOVA showed that plasma treatment ($p=0.688$) and the choice of resin cement ($p=0.353$) had no impact on bond strength results (Table 3). In contrast, the use of adhesive ($p<0.001$) and the aging level ($p<0.001$) significantly affected the SBS. In general, plasma application without pretreatment showed no bonding to PEEK with both tested self-adhesive resin cements regardless of the aging level. The use of Visio.link and Signum PEEK Bond on surfaces treated with and without plasma showed significantly higher SBS values (8.3-15.6 MPa) regardless of aging level. In contrast, the use of Ambarino P60 revealed no bond. Visio.link showed lower initial SBS values with plasma treatment combined with both resin cements and SBS after 5000 thermal cycles with RelyX Unicem Automix 2 than Signum PEEK Bond. No significant impact on SBS between Visio.link and Signum PEEK Bond was observed in all other groups ($p=0.062$-0.572).

Plasma treated groups combined with Signum PEEK Bond showed significantly lower SBS values after 10000 thermal cycles, regardless of the used resin cement.

No cohesive failures were found when the failure types were analyzed (Table 4). Groups without plasma application combined with Visio.link or Signum PEEK Bond showed predominantly mixed failures. Control groups, plasma treated or treated using Ambarino P60 groups fractured predominantly adhesively in all groups.

The SEM evaluation showed – despite polishing – some irregular surface characteristics (Figure 1). Regularly distributed filler fragments were visible at the surface and the PEEK displayed a fissure-like appearance. At higher magnification, plasma application seemed to lead to an accentuated cleft-like matrix formation (Figure 2).

4. Discussion

The effective bonding to PEEK is a prerequisite for its use in dentistry as a prosthetic material. This study evaluated the bond strength of PEEK to two self-adhesive resin cements after plasma application and different primer/adhesive methods after different aging levels. It was shown that neither plasma treatment alone, nor its combination with an adhesive or primer could establish a significant improvement regarding the shear bond strength. Therefore, the null-hypothesis was accepted.

The idea of using a plasma processing technique in order to modify PEEK surfaces has been shown to be a reasonable approach in biomaterials used in trauma, orthopedic and spinal implants [5]. It seems to improve biocompatibility in terms of respective cell to substrate interactions [16-17]. Regarding bonding to materials, plasma application might have different effects due to the fact that PEEK represents mainly an organic thermoplastic polymer material with highly cross-linked structures but a lack of sufficient functional groups being able to react with methacrylate, which are present in most dental composite resin materials. Therefore a limited chemical bonding between these substrates can be expected. However, with plasma treatment, the surfaces of some polymers can be improved in terms of hydrophilicity by forming oxygen-containing functional groups, such as C=O and –OH [18]. Thereby, the composition of the plasma gas should preferably match the chemical structure of the polymer in order to improve the latter's adhesive properties [19]. As for plasma treatment on PEEK in the field of prosthetic dentistry again, data is scarce and recommendations regarding the accurate selection of plasma devices are missing. Using epoxy resins, oxygen as process gas on PEEK may lead to maximum lap shear strength of 34 MPa [20]. Interestingly, the use of air as process gas has been reported to result in slightly lower bond strengths as compared to other process gases [21]. Different resin materials and test conditions might explain these differences. In this study, a cold gas plasma treatment was applied using helium gas. A study by Yavirach and co-workers evaluated the effects of different plasma treatments on the adhesion between fiber-reinforced posts and a composite core build-up material using tensile bond strength tests. The analysis revealed that the type of post, type of plasma treatment, and their interaction significantly influenced the results ($p<0.05$). The study has shown that plasma treatment appeared to increase the tensile-shear bond strength between post and composite. The study used a composite core-build up material based on dimethacrylate and inorganic fillers (MultiCore Flow).

The present study used highly polished PEEK specimens to minimize the micromechanical interference and to focus rather on chemical interactions. Therefore, it was not surprising that no bond could be established on untreated smooth samples using both resin cements without previous application of any adhesive system. However, some surface alterations were observed, which could have led to better penetration of the resin materials in the accentuated gaps forming on the surface after plasma application. But neither the chemical nor these eventually occurring roughening effects of plasma treatment lead to a bonding between the tested materials. This was confirmed in a previous study, which showed that the same self-adhesive cement (RelyX Unicem) was not able to bond to PEEK surfaces even when roughened and sandblasted, except for specimens etched with sulfuric acid, which resulted in slightly higher values as compared to the present study (19.0+/-3.4 MPa). However, no thermocycling was performed in the latter study. Shear bond strength to titanium in the latter study was even lower (8.7+/-2.8 MPa, $p<0.05$), but interestingly, this study showed that an application of an adhesive/composite system (Heliobond/Tetric) enabled bonding to PEEK ranging from 11.5+/-3.2 MPa (silica coating) to 18.2+/-5.4 MPa (acid etched) without statistically significant differences ($p>0.05$). Again, no bond was obtained on the polished surface.

On the other hand, the bond strength cemented with RelyX Unicem to other dental framework materials such as base metal (14.3 MPa), zirconia (16.6 MPa) or lithium disilicate glass-ceramic: (12 MPa) are in the same range of values compared to PEEK combined with Visio.link or Signum PEEK Bond [22].

In this study, the choice of the tested adhesives was based on recommendations of the PEEK manufacturer according to the user's manual, who suggested the use of Visio.link or Ambarino P60 to create sufficient bond strength between PEEK surface and different veneering resin cements. Due to a lack of scientific validation, this study tested whether this statement really applies to self-adhesive resin cements, too. Signum PEEK Bond is an experimental adhesive for bond to PEEK and has therefore been included in this study.

In the present study, we were now able to show that the application of an adhesive prior to the application of a self-adhesive resin cement was able to establish a bonding even after thermal aging and even without air abrasion or sulfur acid application. On the other hand, application of a primer with acidic esters was not able to promote bonding between the substrate and the self-adhesive cement, but rather negatively interfered and hampered bonding efficacy despite the fact that the material contains MMA and dimethacrylate.

In this study, the specimens were tested initially or aged for 5,000 as well as for 10,000 cycles in a thermocycling machine, which corresponds to approx. 4-5-year or 8-10-years period in vivo, respectively [23, 24]. Thermocycling means a repeated cycling between two temperatures (5°C and 55°C) subject to an adequate dwell time (20 s) to ensure the thermal adjustment of the specimens without an exposure to extreme thermal stress [25]. Our measured bond strength results showed an effect only for plasma treated and further conditioned with Signum PEEK Bond groups, regardless of the used resin cements. Other studies also observed an impact of thermocycling on bond strength results [26, 27].

Although in vitro thermocycling subjects all specimens to standardized and reproducible stress, there is no systematic standard procedure for subjecting materials to cycling regimens at present. Thermal loading may lead to mechanical stress on the bonding area, causing volumetric changes. Therefore, cracks can form on the bonding area, caused by the different dimensional changes of the materials [28], which may result in lower values for the bond strength. The chemical composition of Signum PEEK Bond includes MMA and bifunctional monomers based on phosphoric acid esters, while the adhesive system Visio.link based on MMA and PETIA. It could be stated, that the percentage of PETIA and the waiver of acid groups caused in durable bond strength to PEEK. Visio.link in combination with both resin cements showed no negative impact of thermocycling on SBS results. The failure types analysis provided non-differences in fracture modes depending on aging level.

To conclude, plasma application was not able to allow for adequate bonding itself or to improve the bonding performance of the investigated materials. But more studies on this topic are required since plasma deposition methods or coupling agents could be other possibilities to create adhesion sites for a successful establishment or improvement of a bonding between the PEEK substrate and resin materials.

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Conflict of Interest

The authors declare no conflicts of interest.

References:

[1] Tetelman ED, Babbush CA (2008) A new transitional abutment for immediate aestehetics and function. Implant Dent 17:51-58

[2] Santing HJ, Meijer HJ, Raghoebar GM, Ozcan M (2010) Fracture strength and failure mode of maxillary implant-supported provisional single crowns: A comparison of composite resin crowns fabricated directly over PEEK abutments and solid titanium abutments. Clin Implant Dent Relat Res doi: 10.1111/j.1708-8208.2010.00322.x [epub ahead]

[3] Bayer S, Komor N, Kramer A, Albrecht D, Mericske-Stern R, Enkling N (2011) Retention force of plastic clips on implant bars: a randomized controlled trial. Clin Oral Implants Res 2011 doi: 10.111/j.1600-0501.2011.02312.x [epub ahead]

[4] Tannous F, Steiner M, Shahin R, Kern M (2012) Retentive forces and fatigue resistance of thermoplastic resin clasps. Dent Mater 28:273-278

[5] Kurtz SM, Devine JN (2007) PEEK biomaterials in trauma, orthopedic, and spinal implants. Biomaterials 28:4845-4869

[6] Toth JM, Wang M, Estes BT, Scifert JL, Seim HB 3rd, Turner AS (2006) Polyetheretherketone as a biomaterial for spinal applications. Biomaterials 27:324-334

[7] Noiset O, Schneider YJ, Marchand-Brynaert J (2000) Adhesion and growth of CaCo2 cells on surface-modified PEEK substrata. J Biomater Sci Polym Ed 11:767-786

[8] Ohl A, Schröder K, Keller D, Meyer-Plath A, Bienert H, Husen B, Rune GM (1999) Chemical micropatterning of polymeric cell culture substrates using low-pressure hydrogen gas discharge plasmas. J Mater Sci Mater Med 10:747-754

[9] Schmidlin PR, Stawarczyk B, Wieland M, Attin T, Hammerle CH, Fischer J (2010) Effect of different surface pre-treatment and luting materials on shear bond strength to PEEK. Dent Mater 26:553-559

[10] Hallmann L, Mehl A, Sereno N, Hämmerle CHF (2012) The improvement of adhesive properties of PEEK through different pre-treatments. Appl Surf Sci 258:7213-7218

[11] Wegner SM, Gerdes W, Kern M (2012) Effect of different artificial aging conditions on ceramic/composite bond strength. Int J Prosthodont 15:267-72

[12] Kern M. Resin bonding to oxide ceramics for dental restorations (2009) J Adhes Sci Technol 23:1097-111

[13] Kern M, Barloi A, Yang B (2009) Surface conditioning influences zirconia ceramic bonding. J Dent Res 88:817-22

[14] Yang B, Barloi A, Kern M. (2010) Influence of air-abrasion on zirconia ceramic bonding using an adhesive composite resin. Dent Mater 26:44-50

[15] Liston EM. Plasma Treatment for Improved Bonding: A Review (1989) J Adhes 30: 199-218

[16] Schroder K, Meyer-Plath A, Keller D, Ohl A (2002) On the applicability of plasma assisted chemical micropatterning to different polymeric biomaterials. Plasmas and Polymers 7:103–125

[17] Briem D, Strametz S, Schroder K, Meenen NM, Lehmann W, Linhart W, Ohl A, Rueger JM (2005) Response of primary fibroblasts and osteoblasts to plasma treated polyetheretherketone (PEEK) surfaces. J Mater Sci Mater Med 16:671–677

[18] Yavirach P, Chaijareenont P, Boonyawan D, Pattamapun K, Tunma S, Takahashi H, Arksornnukit M (2009) Effects of plasma treatment on the shear bond strength between fiber-reinforced composite posts and resin composite for core build-up. Dent Mater J 28:686-692

[19] Grace JM, Gerenser LJ (2003) Plasma treatment of polymers. J Dispersion Sci Technol 24: 305-341

[20] Comyn J, Mascia L, Xiao G, Parker BM (1996) Plasma-treatment of polyetheretherketone (PEEK) for adhesive bonding. Int J Adhes 16:97-104

[21] Zeiler T (1997) Oberflächenmodifizierung von thermoplastischen Polymerwerkstoffen in Hinblick auf die Verbesserung ihrer Verklebbarkeit. Thesis Erlangen

[22] Sabatini C, Patel M, D'Silva E (2012) In Vitro shear bond strength of three self-adhesive resin cements and a resin-modified glass ionomer cement to various prosthodontic substrates. Oper Dent epub ahead

[23] Pröbster L, Maiwald U, Weber H (1996) Three-point bending strength of ceramics fused to cast titanium. European J Oral Sci 104: 313-319

[24] Leibrock H, Degenhart M, Behr M, Rosentritt M, Handel G (1999) In vitro study on the effect of thermo-and load-cycling on the bond strength of porcelain repair systems. J Oral Rehabil 26: 130-137

[25] Hancox N L (1998) Thermal effect on polymer matrix composites: Part 1. Thermal cycling. Mater Design 19: 85-91

[26] Holderegger C, Sailer I, Schuhmacher C, Schlapfer R, Hammerle C, Fischer J (2008) Shear bond strength of resin cements to human dentin. Dent Mater 24: 944-950

[27] Mazzitelli C, Monticelli F, Toledano M, Ferrari M, Osorio R (2012) Effect of thermal cycling on the bond strength of self-adhesive cements to fiber posts. Clin Oral Investig 16: 909-915

28) Torstenson B, Brannstrom M. Contraction gap under composite resin restorations: effect of hygroscopic expansion and thermal stress. Oper Dent 1988; 13: 24-31.

Table 1

Summary of self-adhesive resin cements and adhesive materials evaluated.

Materials	Product Name	Manufacturer	Composition	Application steps as recommended by the manufacturer	Lot.No	Curing light used
adhesive	Visio.link	Bredent, Senden, Germany	MMA, PETIA, Photoinitiators	1. Apply adhesive on the PEEK surface with a brush 2. Light cure for 90 s	114784	Brelux Power Unit, Bredent
	Signum PEEK Bond I + II (experimental adhesive)	Heraeus Kulzer, Hanau, Germany	Bond I: bifuctional molecules based on phosphoric acid esters and thiol compounds Bond II: MMA, PMMA, Photoinitiators	1. Apply adhesive 1 on PEEK surface and leave for 10 s 2. Apply adhesive 2 and light cure for 90 s	Bond I: 010121 Bond II: 010110	HiLitePower, Heraeus Kulzer
	Ambarino P60	Creamed, Marburg, Germany	Dimethacrylate based on phosphor acidesters and phosphon acidesters	1. Apply on PEEK surface and leave for 120 s	2011004057	
Self-adhesive resin cements	RelyX Unicem Automix 2	3M ESPE, Seefeld, Germany	methacrylated phosphoric esters, dimethacrylate organic fillers	1. light cure for 40	475760	
	Clearfil SA	Kuraray Medical Inc. Sakazu, Kurashiki, Okayama, Japan	Bis-GMA, TEGDMA, MDP, organic fillers	1. light cure for 40	033BBA	

MMA: Methyl methacrylate, PMMA: Polymethyl methacrylate, PETIA: Pentaerythritol thiacrylate, Bis-GMA: Bis phenol A diglycidylmethacrylate, TEGDMA: Triethyleneglycol dimethacrylate, MPD: 10-Methacryloyloxydecyl dihydrogen phosphate

Table 2

SBS (MPa) of the self-adhesive resin cements on polished and differently pre-treated PEEK surfaces.

Plasma pre-treatment	Group	Adhesive	**Cement** *(SBS, MPa)*	
			RelyX Unicem Automix 2	**Clearfil SA**
		initial		
YES	A	Visio.link	12.4 ± 4.3^{b}	8.3 ± 3.3^{b}
	B	Signum PEEK Bond	15.7 ± 3.7^{b}	13.2 ± 4.5^{c}
	C	Ambarino P60	0^{a}	0^{a}
	D	-	0^{a}	0^{a}
NO	A	Visio.link	12.1 ± 3.2^{b}	11.2 ± 3.8^{b}
	B	Signum PEEK Bond	12.7 ± 3.6^{b}	12.8 ± 3.7^{b}
	C	Ambarino P60	0	0
	D	-	0	0
		5000 thermal cycling		
YES	A	Visio.link	11.2 ± 2.9^{b}	12.3 ± 3.6^{b}
	B	Signum PEEK Bond	15.3 ± 4.8^{c}	14.7 ± 5.2^{b}
	C	Ambarino P60	0^{a}	0^{a}
	D	-	0_{a}	0^{a}
NO	A	Visio.link	10.0 ± 2.9^{b}	12.8 ± 2.5^{b}
	B	Signum PEEK Bond	11.7 ± 2.3^{b}	14.3 ± 5.8^{b}
	C	Ambarino P60	0^{a}	0^{a}
	D	-	0^{a}	0^{a}
		10000 thermal cycling		
YES	A	Visio.link	10.8 ± 3.1^{b}	9.7 ± 3.9^{b}
	B	Signum PEEK Bond	9.5 ± 4.2^{b}	10.4 ± 4.2^{b}
	C	Ambarino P60	0^{a}	0^{a}
	D	-	0^{a}	0^{a}
NO	A	Visio.link	11.5 ± 3.4^{b}	11.1 ± 2.5^{b}
	B	Signum PEEK Bond	13.4 ± 4.0^{b}	11.4 ± 2.8^{b}
	C	Ambarino P60	0^{a}	0^{a}
	D	-	0^{a}	0^{a}

^{abc}different letters showed significant differences between the pre-treatment methods among one resin composite, one aging level and with/without plasma treatment.

Table 3

Four-way ANOVA results for comparison of SBS with respect to plasma pretreatment, different adhesives, different resin cements and different aging levels.

	Sum of Squares	df	Mean Squares	F	p-value
Constant parameters	32289	47	687	98	<0.001
plasma treatment	1.13	1	1.13	0.162	0.688
aging level	123	2	62	8.8	<0.001
adhesive	31050	3	10350	1480	<0.001
resin cement	6.0	1	6.0	0.864	0.353
plasma * aging level	77.4	2	38.7	5.5	0.004
plasma * adhesive	31.5	3	10.5	1.5	0.213
plasma * resin cement	27.3	1	27.3	3.9	0.049
aging level * adhesive	224	6	37.4	5.3	<0.001
aging level * resin cement	101	2	50.5	7.2	0.001
adhesive * resin cement	6.7	3	2.2	0.321	0.810
plasma * aging level * adhesive	162	6	30.0	3.9	0.001
plasma * aging level * resin cement	42.4	2	21.2	3.0	0.049
plasma * adhesive * resin cement	32.3	3	10.8	1.5	0.203
aging level * adhesive * resin cement	124	6	20.6	3.0	0.007
Plasma* aging level * adhesive * resin cement	71.4	6	11.9	1.7	0.117
Error	5614	803	7.0		
Total	67894	851			

Table 4

Relative failure type frequencies (95%-confidence intervals in brackets) of all tested groups after SBS tests.

Plasma pre-treatment	Group	Adhesive	Cement *(failure types)* RelyX Unicem Automix 2 *adhesive*	RelyX Unicem Automix 2 *mixed*	RelyX Unicem Automix 2 *cohesive*	Clearfil SA *adhesive*	Clearfil SA *mixed*	Clearfil SA *cohesive*
initial								
YES	A	Visio.link	17 (3-100)	1 (0-27)	0 (0-19)	16 (65-99)	2 (1-35)	0 (0-19)
	B	Signum PEEK Bond	16 (65-99)	2 (1-35)	0 (0-19)	17 (3-100)	1 (0-27)	0 (0-19)
	C	Ambarino P60	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)
	D	-	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)
NO	A	Visio.link	10 (31-79)	8 (22-69)	0 (0-19)	9 (26-74)	9 (26-74)	0 (0-19)
	B	Signum PEEK Bond	10 (31-79)	8 (22-69)	0 (0-19)	8 (22-69)	10 (31-79)	0 (0-19)
	C	Ambarino P60	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)
	D	-	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)
5000 thermal cycles								
YES	A	Visio.link	17 (3-100)	1 (0-27)	0 (0-19)	16 (65-99)	2 (1-35)	0 (0-19)
	B	Signum PEEK Bond	12 (41-87)	3 (4-42)	0 (0-19)	15 (59-97)	3 (4-42)	0 (0-19)
	C	Ambarino P60	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)
	D	-	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)
NO	A	Visio.link	8 (23-69)	10 (31-79)	0 (0-19)	9 (26-74)	9 (26-74)	0 (0-19)
	B	Signum PEEK Bond	10 (31-79)	8 (22-69)	0 (0-19)	8 (22-69)	10 (31-79)	0 (0-19)
	C	Ambarino P60	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)
10000 thermal cycles								
YES	A	Visio.link	17 (3-100)	1 (0-27)	0 (0-19)	16 (65-99)	2 (1-35)	0 (0-19)
	B	Signum PEEK Bond	16 (65-99)	2 (1-35)	0 (0-19)	15 (59-97)	3 (4-42)	0 (0-19)
	C	Ambarino P60	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)
	D	-	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)
NO	A	Visio.link	8 (23-69)	10 (31-79)	0 (0-19)	8 (22-69)	10 (31-79)	0 (0-19)
	B	Signum PEEK Bond	9 (26-74)	9 (26-74)	0 (0-19)	8 (22-69)	10 (31-79)	0 (0-19)
	C	Ambarino P60	18 (81-100)	0 (0-19)	0 (0-19)	18 (81-100)	0 (0-19)	0 (0-19)

Figure 1

SEM-picture of ceramic filled (20% weight) PEEK material.

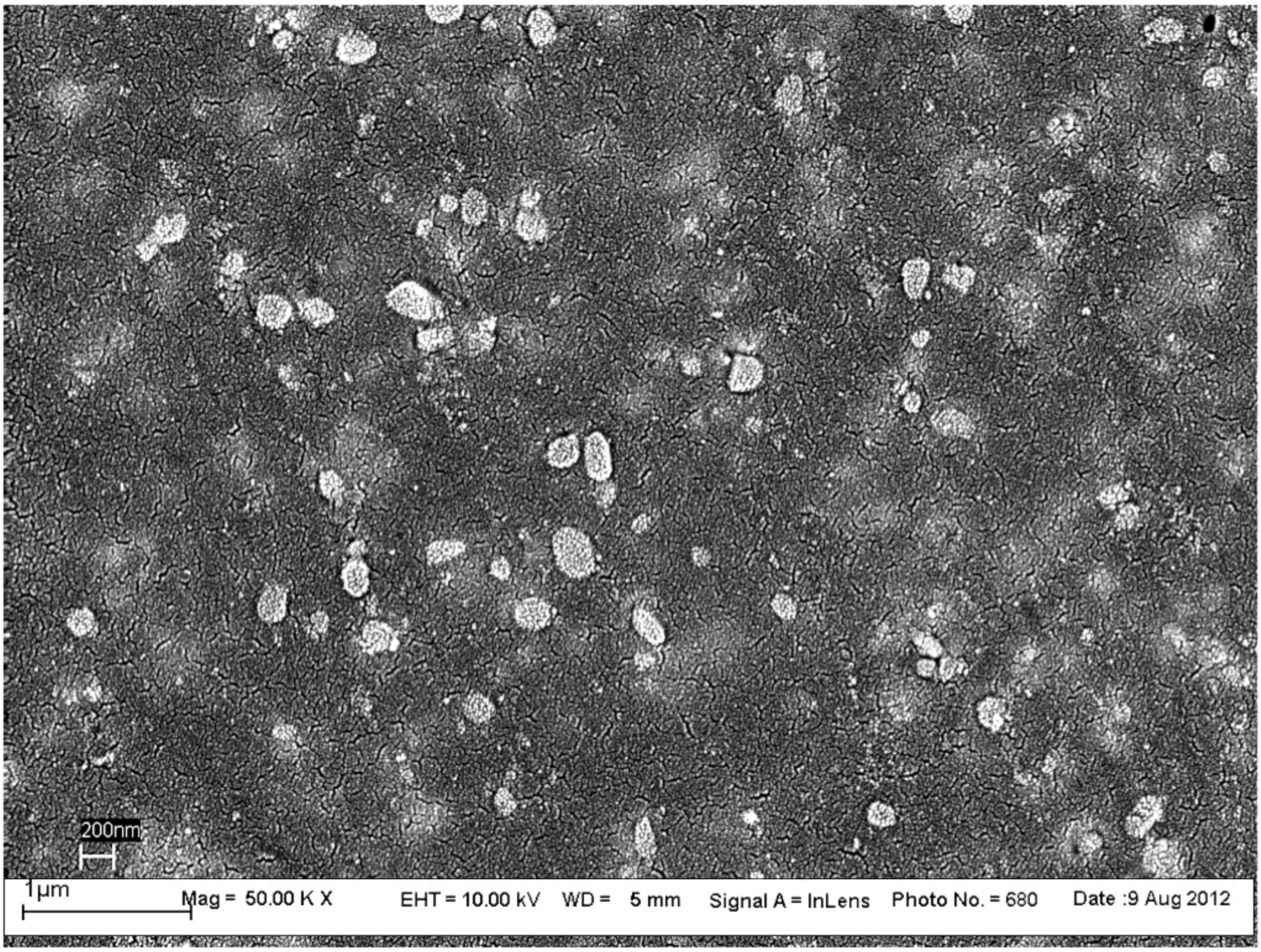

Figure 2

Identical PEEK surface with (left) and without (right) Plasma pre-treatment. The untreated surface was protected from the plasma effect with an adhesive foil, which was later removed for SEM analysis.